

Release of Atrazine and Alachlor from Clay-Oxamide Controlled-Release Formulations†

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Abstract: Controlled-release herbicide formulations have been shown to decrease the leaching potential of several herbicides under laboratory and field conditions. The utility and efficacy of these formulations may be improved by combining several herbicides and a fertilizer source in a single formulation. The objective of these studies was to develop granular alginate formulations that were composed of a combination of the herbicides atrazine and alachlor with the slow-release nitrogen source oxamide (ethanediamide). Controlled release of the herbicides was obtained by addition of selected minerals, including calcium bentonite, fine-grind bentonite, montmorillonite K10, kaolinite and iron (III) oxide. A formulation without clay was used as a comparison. The formulations tested had herbicide active ingredient contents ranging from ~0.02 to 0.54% and a nitrogen content of 21%. Release of the herbicides was studied by equilibrating the formulations with deionized water on a rotary shaker at 200 rev min⁻¹ and sampling at regular time intervals up to 104 hours. The minerals used in the different formulations influenced the herbicide active ingredient composition, as well as the release properties of the individual formulations. The atrazine content of the formulations decreased in the order calcium bentonite > fine-grind bentonite > kaolinite > montmorillonite = iron oxide > no clay. For alachlor the content decreased in the order of calcium bentonite > fine-grind bentonite > montmorillonite > iron oxide > kaolinite > no clay. Controlled release of atrazine (i.e. reduction in release rate) varied in the order calcium bentonite > iron oxide > montmorillonite > fine-grind bentonite = kaolinite > no clay, and for alachlor fine-grind bentonite > calcium bentonite > montmorillonite > no clay = kaolinite = iron oxide. A certain percentage of the applied active ingredient of both alachlor and atrazine was not recovered. From 5 to 27% of the active ingredient was not released, with the greatest retention by the bentonite formulations. Release of nitrogen was not strongly influenced by mineral type, although a trend indicated greater release with formulations containing kaolinite. © 1998 SCI

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Key words: controlled release; herbicides; leaching; groundwater

1 INTRODUCTION

Herbicides are now the leading type of pesticide used in both the US and the world with applications of 252 and 1003 million kg in 1995, respectively.¹ Atrazine and

alachlor are the first and twelfth most widely used herbicides in the US with applications of 31–33 and 7–11 million kg active ingredient in 1995, respectively. Atrazine is a broadleaf herbicide for use in corn and sugarcane and alachlor an annual grass herbicide used in corn, soybeans and peanuts.² It was recently estimated that 160 metric tons of atrazine, 18 metric tons of alachlor and 900 000 metric tons of nitrate were discharged into the Gulf of Mexico from the Mississippi River.^{3,4} The source of this discharge can be traced, to a large extent, to agricultural runoff from the Midwestern

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Cornbelt states of Minnesota, Iowa, and Illinois.⁴ If combined environmental concerns are to be addressed, then alternative agricultural management strategies must be considered.

Recently, increased attention has been directed to the influence of formulation on herbicide environmental fate. Most herbicide formulations in current use deliver the bulk, if not all, of the active ingredient in a labile form that can be readily released to the environment.⁵ In contrast, controlled-release formulations have only a part of the active ingredient in an immediately available form. The bulk of the herbicide is trapped in an inert formulation matrix. After application, the trapped herbicide is gradually released over time, according to the specifications of the controlled-release mechanism. The constituents trapped in the controlled-release matrix (herbicides or fertilizer) would be expected to be less subject to environmental losses.⁶ Several investigators have reported results concerning the effects of controlled-release technologies on herbicide leaching,^{7,8} degradation,^{9,10} runoff¹¹ and volatilization losses.¹³

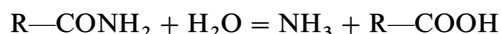
A variety of systems have been used to control herbicide release. These include, alginate encapsulation,^{14,15} lignin entrapment,^{16,17} starch encapsulation^{18–20} and microencapsulation.^{21–23} The majority of these studies developed formulations containing single active constituents (insecticide or herbicide). The one exception is the work of Schreiber *et al.*²⁰ The authors of this study investigated the efficacy of starch-encapsulated formulations containing two or three herbicides. The formulations contained combinations of the herbicides atrazine, alachlor, metolachlor and dicamba. Further advantages would be realized if it were possible to combine a nitrogen source with the controlled-release herbicides, allowing the application of nitrogen and herbicides at the same time. The application could also be made earlier in the season than normal because of the controlled-release properties of both materials.

Considerable research has been conducted on the effects of various clay minerals on pesticide retention and release. The 2:1 phyllosilicate minerals, montmorillonite and bentonite, are both smectites and are characterized by a large surface area and cation exchange capacity (CEC). Kaolinite is a 1:1 phyllosilicate mineral that possesses a relatively low surface area and CEC. Terce and Calvet²⁴ studied the sorption of several pesticides on montmorillonite, illite and kaolinite. Those authors reported that pesticide sorption increased with increasing surface area and CEC of the clay mineral. Fruhstorfer *et al.*²⁵ investigated the adsorption of atrazine on kaolinite and montmorillonite. The authors reported significantly more atrazine sorption on montmorillonite than on kaolinite, with Freundlich *K* values of 41.7 and 2.24 at pH 9.95 and 46.9 and 0.25 at pH 4.5, respectively. The authors are also reported that a significant quantity of the atrazine applied to the montmorillonite system was not

desorbed with water. This was attributed to electrostatic retention of the herbicide in the clay interlayer. Margulies *et al.*²⁶ studied the release of the herbicide EPTC adsorbed to montmorillonite and sepeiolite. The EPTC that was adsorbed to montmorillonite was volatilized at a significantly lower rate than the free herbicide, with half-life ($T_{1/2}$) values of five days compared to 10 h. In addition, the herbicidal activity of the clay-complexed EPTC was extended by more than a week, compared to the free EPTC. Because water molecules will compete with EPTC for sorption sites on montmorillonite,²⁷ the authors first adsorbed the EPTC to a dry soil before adding water. They also stated that the release rate will be strongly dependent on soil moisture content.

Garcia Hernandez *et al.*²⁸ used natural Phillipsite, a zeolitic material, to obtain slow release of oxamyl. The authors reported that a two-stage release of the pesticide from the zeolite complex occurred, with an initial rapid release followed by an extended slow-release stage that lasted for 14 days. Carr *et al.*²⁹ studied the release of the herbicides atrazine and metolachlor from formulations composed of all-starch, all-clay and starch-clay blends. They reported that including clay at levels up to 50% of the total formulation composition had little effect on release or encapsulation efficiency. In contrast, including starch at 20% significantly slowed release rates. Finally, the authors reported that metolachlor was released more rapidly than atrazine.

Oxamide is a slow-release nitrogen source whose agronomic properties have been studied extensively.^{30,31} The material is approximately 32% nitrogen and is only sparingly soluble in water.³² This low solubility gives oxamide its slow-release properties. Nitrogen is released from oxamide in the form of ammonia. The reaction that occurs³⁰ is:



The low solubility of oxamide also made it an attractive choice for alginate formulation, since a nitrogen source with limited solubility in water was needed for mixing with the other formulation components. High solubility in water eliminated the more commonly used fertilizer materials such as urea and ammonium nitrate.

The acceptance and successful performance of controlled-release alginate-based herbicide formulations have been limited by several factors. It has been argued that application of a granular controlled-release product would be uneconomical, requiring additional passes across the field for its application. It was our desire to include a nitrogen source in our herbicide formulations, thus combining application of herbicide and fertilizer and addressing this issue. Our on-going research has also demonstrated that controlled-release formulations that contained linseed oil, at rates greater than 1%, do not release the herbicide fast enough to control the weeds in question adequately. In an attempt

to find a more suitable agent to control herbicide release we have investigated the release properties of various clay minerals. The objectives of this study were: (1) the development of controlled-release formulations containing the herbicides atrazine or alachlor, together with oxamide and selected soil minerals, and (2) the study of the release of the herbicide and nitrogen from the developed formulations.

2 MATERIALS AND METHODS

2.1 Controlled release formulation preparation

Technical grade (TG) atrazine and alachlor were obtained from Ciba-Geigy Inc., Greenville, NC and Monsanto Inc., St. Louis, MO, respectively. Montmorillonite (K10) and iron (III) oxide were obtained from Aldrich Chemical Co., St. Louis, MO. Calcium bentonite and fine-grind bentonite samples were obtained from Dr Richard Zielke, Unimin Research and Development, Spruce Pine, NC. Kaolin, RC-32, AF was obtained from Thiele Kaolin Company, Wrens, Ga. All mineral samples were used without further preparation. Selected properties of the soil minerals are presented in Table 1.

Formulations were prepared to contain 7 g kg^{-1} sodium alginate (Kelgin MV, Kelco, Division of Merck and Company, San Diego, CA), 100 g kg^{-1} oxamide (Aldrich Chemical Co., St. Louis, MO), 33 g kg^{-1} clay or oxide, 3.3 g kg^{-1} 'Tween' 20 (Sigma Chemical Co., St. Louis, MO) and atrazine and alachlor. Controlled-release formulations were prepared by a method similar to that of Pepperman and Kuan,³³ except that the formulation slurry was dropped into the gellant solution (0.25 M CaCl_2) with the aid of a peristaltic pump. The target herbicide active ingredient content for the formulations was 5 g kg^{-1} . This low herbicide level was dictated by the higher formulation application rate ($600\text{--}800 \text{ kg ha}^{-1}$) that would be necessary to achieve adequate N rates when applying the material as a nitro-

gen source. The actual herbicide active ingredient ranged from 1.4 to 5.4 g kg^{-1} for atrazine and 0.2 to 4.7 g kg^{-1} for alachlor. The total nitrogen content of representative formulations was 21%. Herbicide active ingredient was determined by extracting duplicate samples (0.5 g) of each formulation in HPLC grade methanol (100 ml) for 24 h at 200 rev min^{-1} . Extracts were analyzed by solid-phase extraction techniques and high performance TLC methods as described below.

2.2 Release studies

Duplicate samples of each formulation (0.5 g) were weighed into separate 250-ml Erlenmeyer flasks. One hundred milliliters deionized water was added and the flasks were equilibrated on a rotary shaker at 200 rev min^{-1} . At a given sampling point, the flasks were removed from the shaker and the contents of the flask were filtered through Whatman #2 filter paper. The filtered beads were returned to the flasks, deionized water (100 ml) added, and the flasks returned to the shaker. Samples were taken at 1, 2, 4, 8, 24, 32, 48, 56, 72, 80 and 96 h . Sample filtrates were stored at 4°C until analysis by solid phase extraction (SPE) and high performance thin layer chromatography (HPTLC).

2.3 Solid-phase extraction

Solid-phase extraction cartridges (type tC18, Waters Inc., MA) were activated with HPLC methanol (5 ml) and deionized water (5 ml). The sample filtrates (100 ml) were then eluted through the cartridge under vacuum at a rate of approximately 15 ml min^{-1} . After sample loading, the sorbed herbicides were eluted with HPLC methanol (5 ml) into a 7-ml glass vial. All samples were taken to dryness under an air stream and reconstituted in the vial with HPLC methanol ($200 \mu\text{l}$) for analysis by HPTLC.

TABLE 1
Properties of Minerals used in Controlled-Release Formulations

Mineral	Surface area ($\text{m}^2 \text{ g}^{-1}$)	CEC ^a ($\text{meq } 100 \text{ g}^{-1}$)	Surface charge density ^b (meq m^{-2})
Montmorillonite, K10	220–270 ^c	110 ^d	0.50
Calcium bentonite	107 ^c	46.5 ^c	0.43
Fine-grind Bentonite	—	80 ^c	—
Kaolin, RC-32, AF	21 ^c	2.0 ^d	0.095
Iron (III) oxide	34–45 ^d	2–4.0 ^d	0.076

^a Cation exchange capacity.

^b Surface charge density = CEC/Surface area.

^c Experimentally obtained values.

^d Literature values (Reference 42).

2.4 HPTLC

Samples were analyzed for herbicide content by reverse-phase, high performance, thin-layer chromatography.³⁴ Duplicate atrazine and alachlor samples were separated on pre-coated, RP-HPTLC plates (Analtech Inc., Newark, DE), with a mobile phase of methanol + water (70 + 30 by volume). The herbicide concentration on developed plates was determined by comparison with standard curves for both herbicides, which were included on each developed plate. Samples and standard areas were quantified by UV densitometry on a Shimadzu flying spot scanner at 220 nm for atrazine and 200 nm for alachlor.

2.5 Ammonia nitrogen analysis

Selected samples from the release studies were analyzed for ammonia nitrogen with an Orion specific ion electrode. The sample (3 ml) was placed in a 5-ml vial, and immediately prior to analysis, sodium hydroxide (5 M; 1.0 ml) was added, the electrode was inserted in the solution, and the samples were equilibrated while on a stir plate. A reading was automatically taken upon equilibration of the sample. Note that equipment was not available to analyze extracts for oxamide content.

2.6 Total nitrogen analysis

Selected formulations were analyzed for total nitrogen content by the Kjeldahl technique.

3 RESULTS AND DISCUSSION

3.1 Herbicide active ingredient

Differences, albeit small in some cases, were noted in the active ingredient composition of the formulations in response to variation in clay type (Table 2). An equivalent mass of herbicide was added to each formulation;

thus these differences were due to loss of the active ingredient during the formulation process. The losses occurred in several steps, but were most prevalent in the gellation stage, during which the newly formed beads were submerged in a solution of calcium chloride, and in the final rinsing stage when the newly gelled beads were rinsed in deionized water to remove unincorporated herbicide (unpublished data). These losses would be expected to decrease with increased affinity of the herbicide for the formulation. The atrazine active ingredient ranged from 1.4 to 5.4 g kg⁻¹ and was greatest for the formulation containing calcium bentonite, followed by the fine-grind bentonite > kaolinite > montmorillonite = iron oxide > no clay. More distinct differences were observed for alachlor, which ranged from 0.2 to 4.7 g kg⁻¹. The ranking of the formulations was calcium bentonite > fine-grind bentonite > montmorillonite > iron oxide > kaolinite > no clay.

These observed variations are not surprising, considering the expected differences in herbicide retention by the minerals. The two bentonite samples would have a high capacity for herbicide retention due to their large surface areas and CEC (Table 1). As previously stated, Terce and Calvet²⁴ correlated increases in pesticide sorption with increases in surface area and CEC. The slightly lower active ingredient content of the montmorillonite sample is somewhat puzzling. Based on surface area and CEC values, one would predict a higher retention of the active ingredient for both atrazine and alachlor. A possible explanation may be found by examining the effects of surface charge density on pesticide sorption. Laird *et al.*³⁵ have reported that sorption of atrazine decreases with increasing surface charge density. The authors speculated that atrazine is retained as the neutral species and thus will compete with water for sorption sites at the clay surface. Gilchrist *et al.*³⁶ observed a similar trend for sorption of atrazine on sodium and calcium montmorillonite. The authors postulated that, at higher surface charge densities, the water on the clay surface will be tightly bound and possess a highly ordered structure. Atrazine is only sparingly soluble in water and, thus, will not effectively compete for sites on the surface. The montmorillonite sample used in this study has an approximate surface charge density of 0.50 meq m⁻², which is the highest charge density of the minerals investigated. Retention of atrazine by formulations composed of iron oxide or kaolin was similar to that observed for the other 2:1 minerals (Table 2), with active ingredient contents in a similar range to those of other minerals examined. The alachlor active ingredient was significantly lower for iron oxide and kaolinite formulations, indicating greater loss during the formulation process.

The importance of including a mineral to control herbicide release and minimize losses during formulation was clearly demonstrated with the control formulation (i.e. no clay). This formulation also demonstrated that

TABLE 2
Controlled Release Formulation Composition

Formulation	Active ingredient (%)	
	Atrazine	Alachlor
No clay	0.14 (0.004) ^a	0.02 (0.016)
Kaolin	0.50 (0.011)	0.21 (0.002)
Calcium bentonite	0.54 (0.024)	0.47 (0.022)
Fine-grind bentonite	0.53 (0.021)	0.46 (0.020)
Montmorillonite K10	0.49 (0.020)	0.40 (0.050)
Iron (III) oxide	0.49 (0.030)	0.26 (0.007)

^a Standard deviation in parentheses.

the effect of oxamide on herbicide retention was minimal. Previous work³⁷ has also demonstrated that retention of herbicides by formulations containing only alginate are also minimal compared to formulations containing clay. The active ingredient contents of the no-clay formulations were significantly lower than for the mineral formulations, i.e. 1.4 g kg^{-1} for atrazine and 0.2 g kg^{-1} for alachlor. These large formulation losses are probably related to the water solubility of the herbicides and to the sorptive properties of the minerals. The aqueous solubilities of atrazine and alachlor are 33 and $242 \text{ mg liter}^{-1}$, respectively.² The higher water solubility of alachlor would lead to a greater loss of the herbicide during the gellation and rinsing stages of the formulation process. These results show that almost all of the alachlor in the no-clay formulation was lost during the formulation process.

3.2 Herbicide release

Release of atrazine from the formulations was significantly influenced by the mineral type present in the formulation. The greatest reduction in release rates was obtained with the formulation containing calcium bentonite, followed by iron oxide and montmorillonite (Fig. 1). These minerals appeared to have a greater ability to retain atrazine. This increased retention could be explained on the basis of the greater surface area and cation exchange capacity for calcium bentonite and montmorillonite (Table 1). This is not the case, however, for iron oxide, which possesses both a relatively low surface area and CEC. In previous research, iron oxides have been identified as components important in the retention of atrazine in soils.^{38,39} This was the primary

reason for inclusion of iron oxide in our evaluations. Our results appear to confirm the results of these previous studies. Atrazine, a weak base, could protonate and be retained on negative sites on the iron oxide by cation exchange. It is also possible that atrazine could be retained on the oxide *via* hydrogen-bonding mechanisms. Alachlor, a nonionic herbicide, would not be readily retained by the oxide.

The overall ranking of atrazine controlled-release, in terms of herbicide released after 48 h was: calcium bentonite (79%) > iron oxide (86%) > montmorillonite (92%) > fine-grind bentonite (98%) = kaolinite (99%) > no clay (107%). The release pattern for the control formulation is particularly informative and demonstrates the value of including a mineral to control herbicide release. The no-clay formulation released ~85% of its atrazine within 8 h and 100% in 22 h. The highest release level for a mineral formulation after 8 h was 50% (fine-grind bentonite) and the lowest 43% (calcium bentonite). This is compared to 73% and 60% for the fine-grind bentonite and calcium bentonite formulations after 24 h. At the end of the study, the calcium bentonite formulation had released only 83% of the initially applied atrazine. It is possible that the remaining 17% of the herbicide became electrostatically bound in the clay interlayer, and thus would not be readily desorbed by water. All of the applied atrazine was released from the remaining formulations.

The release of alachlor from the formulations exhibited even greater variation due to mineral type (Fig. 2). The greatest control of release was obtained with the formulations containing the fine-grind and calcium bentonites, followed by montmorillonite. As was previously stated, the greater control obtained with these 2:1 minerals is not surprising, considering the

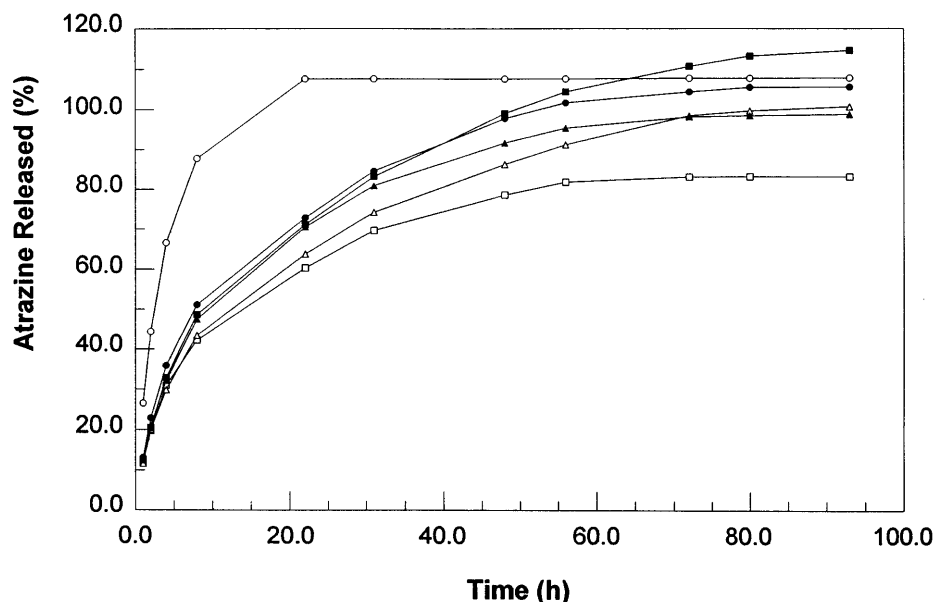


Fig. 1. Release of atrazine from (●) fine-grind bentonite, (■) Kaolin, RC-32, AF, (▲) montmorillonite K10, (○) no clay, (□) calcium bentonite and (△) iron (III) oxide clay-oxamide formulations.

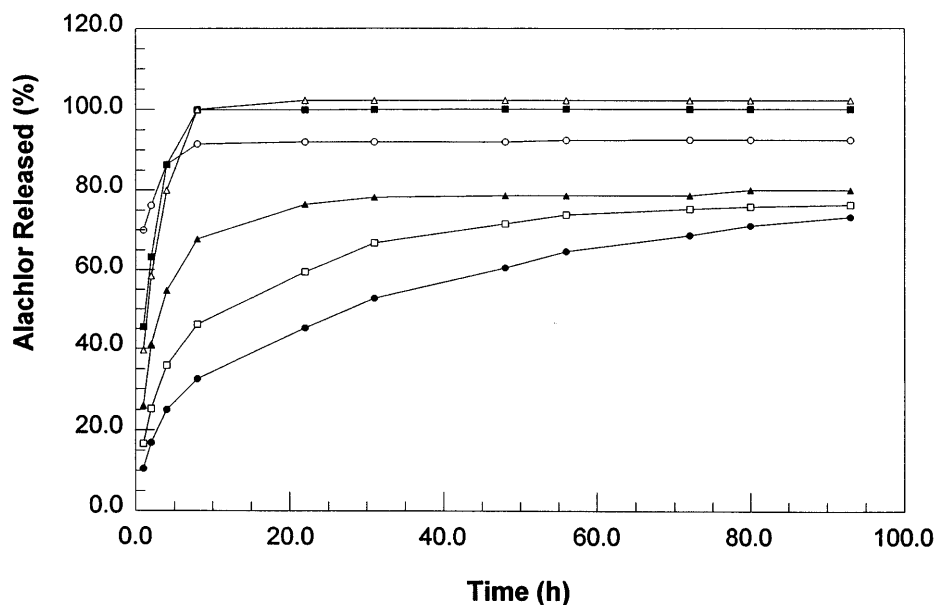


Fig. 2. Release of alachlor from (●) fine-grind bentonite, (■) Kaolin, RC-32, AF, (▲) montmorillonite K10, (○) no clay, (□) calcium bentonite and (△) iron (III) oxide clay-oxamide formulations.

greater surface area and CEC. The slight advantage with the bentonite samples, compared to montmorillonite, is probably related to the effects of surface charge density, as previously discussed. The alachlor in the montmorillonite formulation is probably not retained as strongly as in the bentonite samples due to competition with water molecules for sites on the clay surface. The overall ranking of retention (i.e. control of release) for all formulations was: fine-grind bentonite > calcium bentonite > montmorillonite > no clay = kaolinite = iron oxide. All of the alachlor was released from the kaolinite, iron oxide and no-clay formulations after 8 h, with no difference between these three formulations. This is compared to a release of 33% for the fine-grind bentonite, 46% for the calcium bentonite and 68% for the montmorillonite formulation after 8 h. The fine-grind bentonite formulation performed distinctly differently, in terms of release rates, for atrazine and alachlor. This is perhaps not surprising, owing to the different chemical characters of the two herbicides. Atrazine is a weakly basic compound, while alachlor is nonionic. Also, fine-grind bentonite has a relatively high CEC. It is likely that the fine-grind bentonite formulation is exhibiting a surface charge density phenomenon similar to that for atrazine and montmorillonite. After 104 h, a significant quantity of alachlor had not been released from the fine-grind bentonite, calcium bentonite and montmorillonite formulations. The amount retained was 27% for fine-grind bentonite, 24% for calcium bentonite and 20% for montmorillonite. It is likely that this represents herbicide entrapped in the clay interlayer.

Results from our release studies compare well with those for other controlled-release formulations. Connick¹⁴ was the first to describe controlled-release

herbicide formulations based upon alginate gels. He noted that herbicide release was related to the solubility of the herbicide, the drying time of the gel bead, and the choice of gellant cation. Release of 2,4-D was controlled for four to six days with Ca-gelled beads and 14 days with Ba-gelled beads. In a later study,³⁷ the value of including kaolin as a filler in alginate controlled-release formulations of 2,6-dichlorobenzonitrile was demonstrated. Formulations that contained kaolin increased formulation yield by 13-fold and extended release over 2-fold, compared to formulations without kaolin. Pepperman *et al.*¹⁵ reported that replacing some of the kaolin in alginate formulations with other adsorbents (i.e. alumina, silica gel, celite) did not improve the release of metribuzin. Addition of charcoal to the formulations extended the release time, but some of the herbicide was irreversibly sorbed. A later study⁴⁰ demonstrated that linseed oil could be used to extend the release of metribuzin significantly. Davis *et al.*⁴¹ studied the release from commercial and controlled-release formulations of fenamiphos, atrazine, and alachlor in a dynamic, flow-through system. The authors indicated that the pesticide's aqueous solubility and lipophilicity had a significant effect on both the release rate and the total amount of herbicide released. Starch-encapsulated formulations released from 5 to 94% of the applied herbicide in 24 h and alginate formulations from 0.3 to 100%. Alginate formulations that contained both kaolin and linseed oil released insignificant amounts of atrazine (0.3%) and small amounts of alachlor (12%) in 24 h. This later observation agrees with results from field evaluations of alginate-kaolin-linseed oil formulations of atrazine and metribuzin. Inclusion of linseed oil in metribuzin and atrazine formulations at rates greater than 1% slowed release to unacceptable

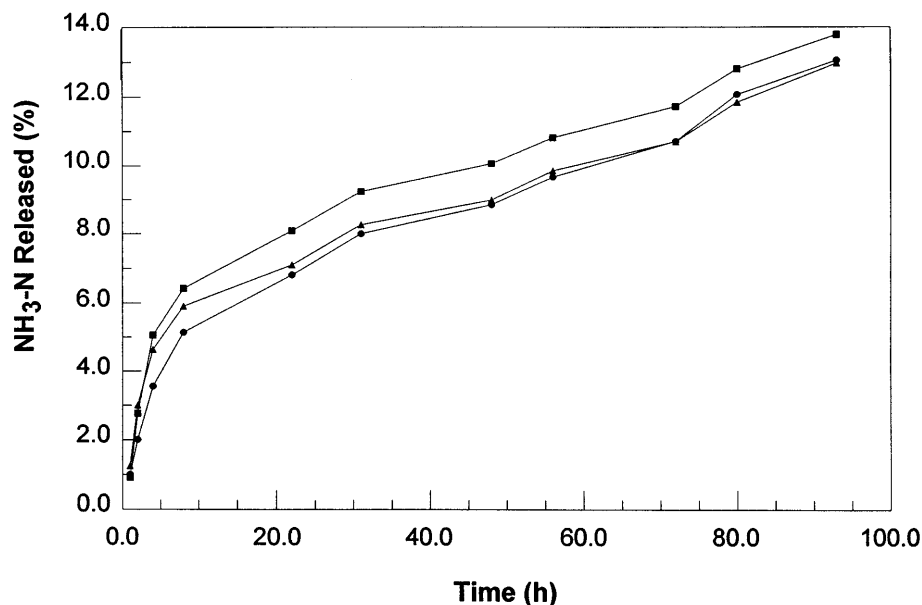


Fig. 3. Release of ammonia nitrogen from (●) fine-grind bentonite, (■) Kaolin, RC-32, AF and (▲) montmorillonite K10 clay-oxamide formulations.

levels (Johnson, Pepperman and Selim, unpublished). As previously stated, this was one of the justifications for development of the oxamide-clay-based formulations described in this paper.

3.3 Nitrogen release

Release of ammonia nitrogen was investigated for only selected formulations (fine-grind bentonite, montmorillonite, kaolinite). As previously stated, it was not possible to analyze the samples directly for oxamide content. It should also be noted that ammonia is a plant-available form of nitrogen whereas oxamide would not be readily available for uptake. There was no significant difference in nitrogen release due to mineral type, although there appeared to be a slight advantage with the 2:1 minerals, fine-grind bentonite and montmorillonite, compared to kaolinite (Fig. 3). In the duration of the experiment, an average of 14% of the added nitrogen was released as ammonia. Further studies would be needed to characterize more completely the nitrogen-release characteristics of these formulations, particularly in soil systems where conversion of oxamide to ammonia would be encouraged.

4 CONCLUSIONS

Controlled-release formulations containing atrazine, alachlor, oxamide, and selected soil minerals were prepared. Distinct differences in release of both herbicides were observed with variations in the mineral type. The 2:1 phyllosilicate minerals calcium bentonite, fine-grind bentonite, and montmorillonite resulted in formulations with the greatest control of release and least

losses during the formulation process. A distinct quantity of alachlor, and to a lesser extent atrazine, was not released from the calcium bentonite, fine-grind bentonite, and montmorillonite formulations. Based on these observations the calcium bentonite formulation would appear to offer the best combination of controlled release and AI properties. It is likely that herbicide (atrazine or alachlor) trapped in the clay interlayer would not be readily released. The release of nitrogen from the formulations appears not to be strongly controlled by mineral type. Gradual release of ammonia was observed for the all formulations investigated, amounting to approximately 12–14% during the course of the experiment.

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